Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

threo-1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol

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Received 8 March 2002
Accepted 14 March 2002
Online 22 March 2002

In the crystals of the lignin model, *threo*-1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol, $C_{18}H_{22}O_6$, the molecules adopt a conformation in which the $C_{aryl}\cdots C_{aryl}$ distance between the bulky 2-methoxyphenyl and 3,4-dimethoxyphenyl groups, 4.871 (3) Å, is very close to the calculated maximum value, 4.88 Å. The torsion angle between the 2-methoxyphenoxy group and the 3,4-dimethoxyphenyl group is 176.02 (19)°. Intermolecular hydrogen bonding between benzylic hydroxyl groups results in a helical arrangement of the molecules in the crystals.

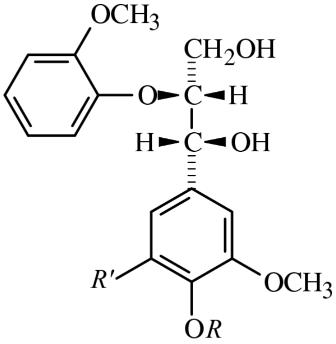
Key indicators

Single-crystal X-ray study
T = 183 K
Mean σ(C–C) = 0.004 Å
R factor = 0.065
wR factor = 0.175
Data-to-parameter ratio = 13.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Arylglycerol β-aryl ethers constitute a major type of linkage between phenylpropane units in lignins. 1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol, (I), is frequently used as a model compound representative of such structural elements. This compound was originally synthesized by Adler *et al.* (1952). Gierer & Norén (1962) described the *erythro* and *threo* (I) forms. The assignments were confirmed in later studies (Stomberg & Lundquist, 1994, and references therein).



(I) $R = CH_3$, $R' = H$
(II) $R = H$, $R' = OCH_3$
(III) $R = R' = H$

In conjunction with studies of the conformation of model compounds for different types of arylglycerol β-aryl ethers (Langer *et al.*, 2002), we have now determined the crystal structure of (I). A perspective drawing of the molecule and the atom-numbering scheme is shown in Fig. 1. Stereochemically pure (I) was separated from a mixture of the diastereomers by ion-exchange chromatography using a borate solution as the eluent (*cf.* Li *et al.*, 1994). The fraction of (I) obtained crystallized on standing. The crystalline form of (I) has not been described previously.

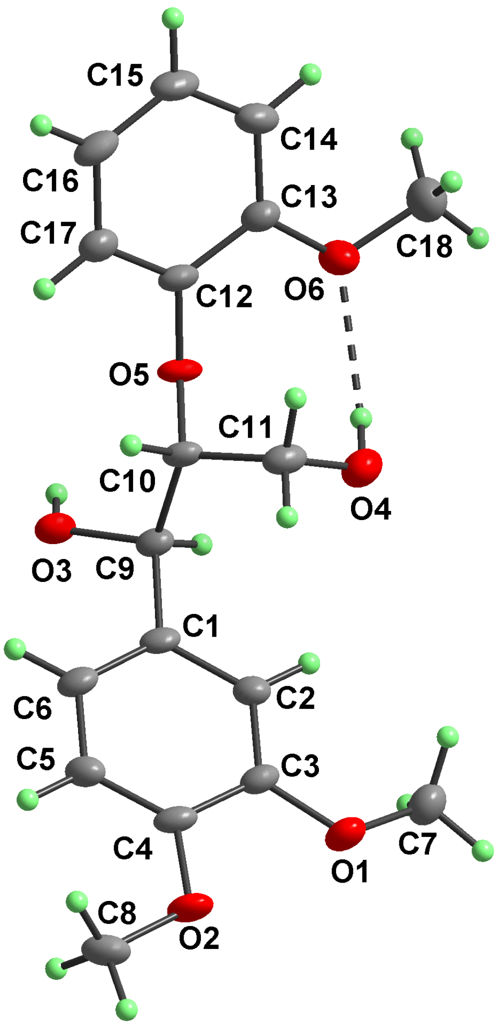


Figure 1
The atom-numbering scheme for (I). Displacement ellipsoids are shown at the 50% probability level. A broken line shows the intramolecular hydrogen bond.

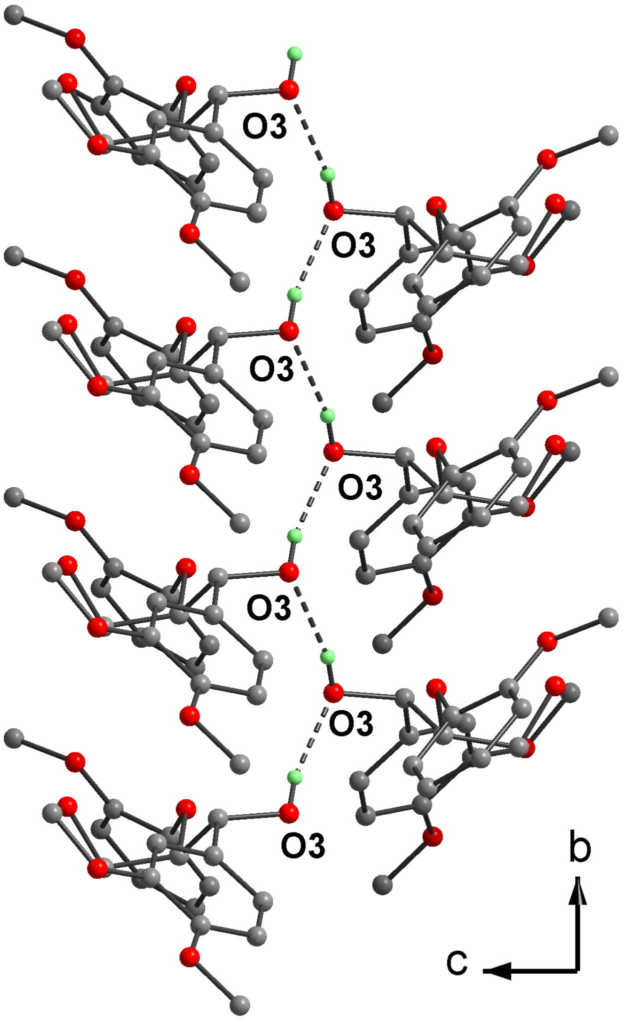


Figure 2
The intermolecular hydrogen-bonding pattern. H atoms (with the exception of HO3) have been omitted for clarity.

Compound (I) adopts a conformation in which the bulky aromatic groups are almost as far apart as possible. The torsion angle C12—O5—C10—C9 is 165.07 (19)° and the torsion angle C1—C9—C10—O5 is 176.02 (19)°. This leads to a C1···C12 distance of 4.871 (3) Å. The calculated maximum value is 4.88 Å. The dihedral angle between the aromatic ring planes is 48.68 (9)°. Crystal structures of two models of the same type as (I) (*threo* forms of arylglycerol β-guaiacyl ethers) have previously been determined, namely (II) (Stomberg *et al.*, 1988) and (III) (Lundquist *et al.*, 1996). The conformations of (II) and (III) resemble that of (I). The torsion angle C12—O5—C10—C9 in (I) is, however, smaller in (II) [126.3 (3)°] and (III) [120.1 (4)°]. As a consequence of this, the distance corresponding to C1···C12 in (I) is smaller in these compounds: 4.773 (4) Å in (II) and 4.733 (5) Å in (III).

There is an intramolecular hydrogen bond in (I), formed by HO4 and atoms O4 and O6 (Fig. 1 and Table 1). Intermolecular hydrogen bonding involving the benzylic hydroxyl group, O3—HO3···O3, leads to a helical arrangement of the molecules in the crystal structure in the direction of the monoclinic unique *b* axis (Fig. 2).

The conformations of lignin model compounds of the arylglycerol β-aryl ether type have been subjected to computational studies. According to recent calculations, *threo* forms of arylglycerol β-guaiacyl ethers can be expected to adopt extended conformations with the aromatic groups well separated (Simon & Eriksson, 1998; Besombes *et al.*, 2001). Interestingly, this is the case in the crystal structures of the *threo*-arylglycerol β-guaiacyl ethers (I)–(III).

Experimental

Compound (I) was synthesized according to Ibrahim & Lundquist (1994) (see also Li *et al.*, 1995). Separation of the diastereomers was accomplished by ion-exchange chromatography (*cf.* Li *et al.*, 1994). Crystals of the *threo* form, suitable for X-ray crystallography, were obtained from ethyl acetate (m.p. 345–347 K).

Crystal data

$C_{18}H_{22}O_6$
$M_r = 334.36$
Monoclinic, $P2_1/c$
$a = 13.7932$ (2) Å
$b = 4.6909$ (1) Å
$c = 25.2138$ (3) Å
$\beta = 93.064$ (1)°
$V = 1629.06$ (5) Å^3
$Z = 4$

$D_x = 1.363$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6757 reflections
$\theta = 2.1$–26.6°
$\mu = 0.10$ mm^{-1}
$T = 183$ (2) K
Needle, colourless
0.55 × 0.05 × 0.05 mm

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
$T_{\min} = 0.946$, $T_{\max} = 0.995$
15921 measured reflections

3375 independent reflections
2422 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.077$
$\theta_{\max} = 26.6°$
$h = -17 \rightarrow 17$
$k = -5 \rightarrow 5$
$l = -31 \rightarrow 31$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.065$
$wR(F^2) = 0.175$
$S = 1.06$
3375 reflections
244 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0874P)^2 + 1.0506P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.29$ e Å^{-3}
$\Delta\rho_{\min} = -0.39$ e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O3$^{\rm i}$	0.84	2.01	2.8293 (18)	165
O4—H4···O6	0.84	2.21	2.974 (3)	152
C7—H7*A*···O2$^{\rm ii}$	0.98	2.60	3.406 (4)	140
C15—H15···O2$^{\rm iii}$	0.95	2.57	3.356 (3)	140
C17—H17···O3$^{\rm iv}$	0.95	2.58	3.492 (3)	162
C18—H18*B*···O4$^{\rm v}$	0.98	2.40	3.351 (4)	165

Symmetry codes: (i) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$; (ii) $x, 1+y, z$; (iii) $1+x, y, z$; (iv) $1-x, y-\frac{1}{2}, \frac{3}{2}-z$; (v) $1-x, 2-y, 1-z$.

H atoms were refined isotropically and were constrained to the ideal geometry using an appropriate riding model. For hydroxyl groups, the O—H distances (0.84 Å) and C—O—H angles (109.5°) were kept fixed, and the torsion angle was chosen to maximize the electron density. For methyl groups, the C—H distances (0.98 Å) and C—C—H angles (109.5°) were kept fixed, while the torsion angles were allowed to refine with the starting position based on a threefold averaged circular Fourier synthesis.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT* and *SADABS* (Sheldrick, 2001); program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *SHELXTL*.

References

Adler, E., Lindgren, B. O. & Saedén, U. (1952). *Sven. Papperstidn.* **55**, 245–255.

Besombes, S., Mazeau, K., Robert, D., Taravel, F. R. & Utille, J. P. (2001). *Proceedings of the 11th International Symposium on Wood and Pulping Chemistry*, June 11–14, Nice, France. Vol. III, pp. 581–584.

Brandenburg, K. (2000). *DIAMOND*. Version 2.1d. Crystal Impact GbR, Bonn, Germany.

Bruker (1997). *SHELXTL* (Version 5.10). Bruker AXS Inc., Madison, Wisconsin, USA.

Gierer, J. & Norén, I. (1962). *Acta Chem. Scand.* **16**, 1976–1988.

Ibrahim, W. & Lundquist, K (1994). *Acta Chem. Scand.* **48**, 149–151.

Langer, V., Lundquist, K., Stomberg, R. & von Unge, S. (2002). *Acta Cryst.* E**58**, o90–o92.

Li, S., Lundquist, K. & Paulsson, M. (1995). *Acta Chem. Scand.* **49**, 623–624.

Li, S., Lundquist, K. & Soubbotin, N. (1994). *Holzforschung*, **48**, 509–511.

Lundquist, K., Li, S. & Stomberg, R. (1996). *Nord. Pulp Pap. Res. J.* **11**, 43–47.

Simon, J. P. & Eriksson, K. E. L. (1998). *Holzforschung*, **52**, 287–296.

Sheldrick, G. M. (2001). *SADABS*. University of Göttingen, Germany.

Siemens (1995). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Stomberg, R., Hauteville, M. & Lundquist, K. (1988). *Acta Chem. Scand. Ser. B*, **42**, 697–707.

Stomberg, R. & Lundquist, K. (1994). *Nord. Pulp Pap. Res. J.* **9**, 37–43.